



PCT/AU03/01330

#12

REC'D 27 OCT 2003

WIPO PCT

Patent Office  
Canberra

**PRIORITY  
DOCUMENT**

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND  
SALES hereby certify that annexed is a true copy of the Provisional specification  
in connection with Application No. 2002951962 for a patent by BHP BILLITON  
INNOVATION PTY LTD as filed on 09 October 2002.



WITNESS my hand this  
Twenty-second day of October 2003

*J. Billingsley*

JULIE BILLINGSLEY  
TEAM LEADER EXAMINATION  
SUPPORT AND SALES

AUSTRALIA  
Patents Act 1990

PROVISIONAL SPECIFICATION

Applicant(s):

BHP BILLITON INNOVATION PTY LTD  
A.C.N. 008 457 154

Invention Title:

ELECTROLYTIC REDUCTION OF METAL OXIDES

The invention is described in the following statement:

## ELECTROCHEMICAL REDUCTION OF METAL OXIDES

The present invention relates to electrochemical reduction of metal oxides.

5

The present invention was made during the course of an on-going research project on the electrochemical reduction of titania ( $\text{TiO}_2$ ) carried out by the applicant.

10

During the course of the research project the applicant carried out experimental work on an electrolytic cell that included a graphite crucible that formed an anode of the cell, a pool of molten  $\text{CaCl}_2$ -based electrolyte in the crucible, and a cathode that included solid titania.

15

The  $\text{CaCl}_2$ -based electrolyte was a commercially available source of  $\text{CaCl}_2$ , namely calcium chloride dihydrate, that decomposed on heating and produced a very small amount of  $\text{CaO}$ .

20

The applicant operated the electrolytic cell at a potential above the decomposition potential of  $\text{CaO}$  and below the decomposition potential of  $\text{CaCl}_2$ .

25

The applicant found that the cell could electrochemically reduce titania to titanium with very low concentrations of oxygen.

30

The applicant does not have a clear understanding of the electrolytic cell mechanism at this stage. Nevertheless, whilst not wishing to be bound by the comments in this paragraph, the applicant offers the following comments by way of an outline of a possible cell mechanism. The experimental work carried out by the applicant produced evidence of Ca metal dissolved in the electrolyte. The applicant believes that, at least during

35

the early stages of operation of the cell, the Ca metal was the result of electrodeposition of  $\text{Ca}^{++}$  cations as Ca metal on electrically conductive sections of the cathode. As is indicated above, the experimental work was carried  
5 out using a  $\text{CaCl}_2$ -based electrolyte at a cell potential below the decomposition potential of  $\text{CaCl}_2$ . The applicant believes that the initial deposition of Ca metal on the cathode was due to the presence of  $\text{Ca}^{++}$  cations and  $\text{O}^{--}$  anions derived from  $\text{CaO}$  in the electrolyte. The  
10 decomposition potential of  $\text{CaO}$  is less than the decomposition potential of  $\text{CaCl}_2$ . In this cell mechanism the cell operation is dependent, at least during the early stages of cell operation, on decomposition of  $\text{CaO}$ , with  
15  $\text{Ca}^{++}$  cations migrating to the cathode and depositing as Ca metal and  $\text{O}^{--}$  anions migrating to the anode and forming CO and/or  $\text{CO}_2$  (in a situation in which the anode is a graphite anode). The applicant believes that the Ca metal that deposited on electrically conductive sections of the cathode was deposited predominantly as a separate phase in  
20 the early stages of cell operation and thereafter dissolved in the electrolyte and migrated to the vicinity of the titania in the cathode and participated in chemical reduction of titania. The applicant also believes that at later stages of the cell operation part of the Ca metal  
25 that deposited on the cathode was deposited directly on partially deoxidized titanium and thereafter participated in chemical reduction of titanium. The applicant also believes that the  $\text{O}^{--}$  anions, once extracted from the titania, migrated to the anode and reacted with anode  
30 carbon and produced CO and/or  $\text{CO}_2$  and released electrons that facilitated electrolytic deposition of Ca metal on the cathode.

However, notwithstanding that the cell could  
35 electrochemically reduce titania to titanium with very low concentrations of oxygen, the applicant also found that there were relatively significant amounts of carbon

transferred from the anode to the electrolyte and to the titanium produced at the cathode under a wide range of cell operating conditions. Carbon in the titanium is an undesirable contaminant. In addition, carbon transfer was responsible for low current efficiency of the cell. Both problems are significant barriers to commercialisation of the electrochemical reduction technology.

The applicant carried out experimental work to identify the mechanism for carbon transfer and to determine how to minimise carbon transfer and/or to minimise the adverse effects of carbon transfer.

In the course of the experimental work the applicant made the invention that is described and claimed in International application PCT/AU02/00457 in the name of the applicant. The invention minimises carbon contamination by replacing the carbon anode with a molten metal anode.

In broad terms, the invention that is described and claimed in the International application provides an electrolytic cell for electrochemical reduction of a metal oxide, such as titania, in a solid state, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode formed at least in part from the metal oxide in contact with the electrolyte, and (c) a molten metal anode in contact with the electrolyte.

In addition, in broad terms the invention that is described and claimed in the International application is a method of electrochemically reducing a metal oxide, such as titania, in a solid state in an electrolytic cell, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode in contact with the electrolyte, the cathode being formed at least in part from the metal oxide, and (c) a molten metal anode in contact with the electrolyte,

and which method includes applying a cell potential across the anode.

5 The present invention is an improvement of the invention described and claimed in the International application.

10 According to the invention there is provided an electrolytic cell for electrochemical reduction of a metal oxide, such as titania, in a solid state, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode formed at least in part from the metal oxide in contact with the electrolyte, (c) an anode, and (d) a membrane that separates the electrolyte and the anode and  
15 is permeable to oxygen cations and is impermeable to dissolved metal in the electrolyte, and optionally is impermeable to any one or more of (i) electrolyte anions other than oxygen anions, (ii) anode metal cations, and (iii) any other ions and atoms.

20

The above-described membrane prevents back reaction of dissolved metal in the electrolyte and oxygen atoms generated at the anode that can significantly reduce the current efficiency of the cell. Specifically, the  
25 membrane allows oxygen anions to migrate to the anode and give up electrons at the anode and prevents dissolved metal in the electrolyte migrating to the anode and reacting with oxygen atoms generated at the anode.

30 Accordingly, the membrane makes it possible for the cell to operate at high current efficiencies

In a situation in which the membrane is also impermeable to electrolyte anions other than oxygen  
35 anions, the membrane makes it possible to operate the cell at higher potentials without the disadvantages that are often associated with operating at such higher cell

potentials. For example, in situations in which the electrolyte includes  $\text{CaCl}_2$ , it is undesirable to operate at potentials that result in evolution of chlorine gas because of the corrosive and toxic properties of the gas.

5 The membrane prevents the migration of  $\text{Cl}^-$  anions to the anode and thereby prevents the evolution of chlorine gas. Operating at higher cell potentials is advantageous because it produces higher currents and therefore reduces cycle times.

10

In a situation in which the membrane is also impermeable to anode metal cations it is possible to use anode materials that would react with the electrolyte save for the membrane separating the anode and the electrolyte.

15 Thus, there is a wider selection of anode materials that are available.

Preferably the anode is a molten metal anode.

20

However, the present invention also extends to other arrangements. For example, the present invention extends to fuel cell arrangements in which there is (a) a coating of a suitable metal/metal oxide system, such as  $\text{Ni/NiO}$ , on the membrane that forms the anode and conducts  
25 electrons released by the oxygen anions and (b) a fuel, such as hydrogen or natural gas, that consumes oxygen that is evolved at the anode.

The anode may be arranged so that oxygen gas is  
30 evolved at the anode and is removed from the cell.

The anode may be also be arranged so that there is no oxygen gas released from the anode assembly. Specifically, the anode may include a means for scavenging  
35 oxygen that is generated at the anode when oxygen anions migrate to the anode and give up electrons at the anode. The above-described gaseous fuel is one suitable

scavenging means. The scavenging means may also be a solid material that is oxidised by oxygen.

5 The use of solid scavenging materials is preferred in situations in which the anode is a molten metal anode. Suitable solid materials for molten silver anodes include iron, carbon and tungsten. The use of a scavenging means reduces the need to select molten metal anodes that have high solubility of oxygen in anode metal.

10

Preferably the solid scavenging materials form the anode electrode for molten metal anodes.

15 It is preferred that the membrane be impermeable to the anode electrode material.

The present invention is based on experimental work carried out by the applicant to electrochemically reduce titania. The experimental work was carried out on  
20 a cell that includes a stainless steel crucible containing molten  $\text{CaCl}_2$ -based electrolyte containing at least some  $\text{CaO}$ , a cathode extending into the electrolyte, the cathode including  $\text{TiO}_2$ , and an anode in the form of molten silver contained in a yttria stabilised zirconia crucible  
25 extending into the electrolyte. The yttria stabilised zirconia is permeable to oxygen anions and is impermeable to calcium metal dissolved in the electrolyte, chlorine anions, and silver cations. The anode electrical connection was made via a low carbon steel wire extending  
30 into the molten silver. The cell was operated initially at a potential around 3V. It was found that oxygen was removed from the cell - by oxidation of the steel electrode - under these conditions at high current efficiencies. Operation at high current efficiencies  
35 indicated that there was no back reaction of calcium metal and oxygen generated at the anode. The cell was also operated at higher potentials, up to 10V. It was found



that there was decomposition of  $\text{CaCl}_2$  and no evolution of chlorine gas under these conditions. There was also a proportional increase in current with increasing voltage.

The experimental work opens up the following possibilities for an electrolytic cell for electrochemically reducing metal oxides, such as titania:

- Operating the cell at high current efficiencies - with minimal back reaction.
- Operating the cell at high voltages resulting in high currents, and thereby reducing cycle time.
- Operating the cell with an oxygen scavenger in the anode assembly, thereby eliminating difficulties with handling oxygen gas at high temperatures. Scavengers for molten silver anodes include iron, carbon, and tungsten.
- Alternatively, operating the cell with an anode that generates oxygen gas and removing oxygen gas from the anode assembly.

In a situation in which the anode is a molten metal anode, preferably the metal is chosen such that its melting point is within the operating temperature range of the electrolyte.

Preferably the melting point of the metal of the molten metal anode is higher than the melting point of the electrolyte and lower than the vaporisation and/or decomposition temperature of the electrolyte in order to prevent electrolyte consumption and removal through vaporisation.

Preferably the metal of the molten metal anode is

silver or copper.

Preferably the membrane is formed from a solid electrolyte.

5

Preferably the solid electrolyte is an oxide.

More preferably the solid electrolyte is yttria stabilised zirconia.

10

Preferably the membrane includes a body and an outer lining, with the outer lining being in contact with the electrolyte, and the outer lining being formed from a material that is inert with respect to dissolved metal in the electrolyte and is impermeable to the dissolved metal.

15

In a situation in which the metal oxide is titania it is preferred that the electrolyte be a  $\text{CaCl}_2$ -based electrolyte that includes  $\text{CaO}$  as one of the constituents. In this situation calcium metal will be the dissolved metal in the electrolyte.

20

Preferably the body is formed from the solid electrolyte.

25

Preferably the outer lining is formed from a rare earth oxide.

More preferably the rare earth oxide is yttria.

30

Preferably the lining is continuous and covers all of the surface of the membrane that is in contact with the electrolyte so that there are no sections of the body that are in contact with the electrolyte.

35

Preferably the metal oxide is a titanium oxide.

It is preferred that the metal oxide be titania.

According to the present invention there is also provided a method of electrochemically reducing a metal  
5 oxide in a solid state in an electrolytic cell, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode in contact with the electrolyte, the cathode being formed at least in part from the metal oxide, (c) an anode, and (d) a membrane that separates the electrolyte  
10 and the anode and is permeable to oxygen ions and is impermeable to dissolved metal in the electrolyte, and optionally is impermeable to any one or more of (i) electrolyte anions other than oxygen anions, (ii) anode metal cations, and (iii) any other ions and atoms, and  
15 which method includes applying a cell potential across the anode and the cathode and electrochemically reducing the metal oxide.

Preferably, in a situation in which the metal  
20 oxide is titania, the method includes electrochemically reducing the metal oxide to titanium having an oxygen concentration of less than 0.2wt. %.

Preferably the method includes maintaining the  
25 cell temperature below the vaporisation and/or decomposition temperatures of the electrolyte.

Preferably the method includes applying a cell potential above a decomposition potential of at least one  
30 constituent of the electrolyte so that there are cations of a metal other than that of the cathode metal oxide in the electrolyte.

Preferably the membrane is formed from a solid  
35 electrolyte.

Preferably the solid electrolyte is yttria

stabilised zirconia.

Preferably the metal oxide is a titanium oxide.

5 It is preferred that the metal oxide be titania.

In a situation in which the metal oxide is  
titania it is preferred that the electrolyte be a  $\text{CaCl}_2$ -  
based electrolyte that includes  $\text{CaO}$  as one of the  
10 constituents.

In such a situation it is preferred that the  
method includes maintaining the cell potential above the  
decomposition potential for  $\text{CaO}$ .

15

The following example illustrates an application  
of the invention in the process of reducing titania into  
substantially pure titanium using an electrolytic cell  
constructed in accordance with the present invention and  
20 as illustrated schematically in Figure 1.

Whilst the example described below relates to the  
electrochemical reduction of titania, the basic principle  
is equally applicable to other metal oxides, in particular  
25 oxides of Si, Ge or alloys containing these metals.

With reference to the figure, the electrolytic  
cell 2 includes a graphite-free crucible 10 made of a  
suitable refractory material that is essentially inert  
30 with respect to the electrolyte and electrode materials  
described below at cell operating temperatures.

The electrolytic cell further includes a pool 18  
of molten  $\text{CaCl}_2$  electrolyte that contains at least some  $\text{CaO}$   
35 within the crucible 10.

The electrolytic cell 2 further includes a pool

14 of molten silver or copper contained in a crucible of yttria stabilised zirconia that extends into the cell. The molten Ag or Cu forms the molten metal anode 14 of the cell. The yttria stabilised zirconia crucible 16 forms a  
5 membrane that allows migration of oxygen anions and prevents migration of calcium metal dissolved in the molten electrolyte into the molten anode. Optionally, the crucible has an outer lining of yttria.

10 The electrolytic cell 2 further includes a titania plate 12 positioned within a cage 24. The cage 24 (and therefore the plate 12) is suspended into the crucible 10 by means of a lead 26. This assembly forms the cathode 20 of the cell.

15

The electrolytic cell 2 further includes a power source 22 and electrical connections between the power source 22 and the anode 14 and the cathode 20. The connections include the above-described lead 26 and a  
20 further electrical lead 28. The electrical lead 28 is a low carbon steel wire that is consumed during the operation of the cell - as described below.

In use, power source 22 provides constant  
25 potential (voltage) settings thereby that allow the cell 2 to draw the amount of current required during the electrolytic refining of the metal oxide body at a selected potential.

30 The electrolytic cell 2 further includes thermocouples contained in suitable heat-resistant, inert sheaths (not illustrated) for monitoring temperature in the molten metal anode 14 and the molten electrolyte 18.

35 In use, the above-described electrolytic cell 2 is positioned in a suitable furnace to maintain the electrolyte and the anode metal in their respective molten

states. The atmosphere around the crucible 10 is preferred to be an inert gas, such as argon, that does not react with the molten electrolyte.

5           Once the cell reaches its operating temperature, a preselected voltage above the decomposition potential of  $\text{CaO}$  in the electrolyte is applied to the cell, whereby reduction of the titania in the cathode is carried out as described above.

10

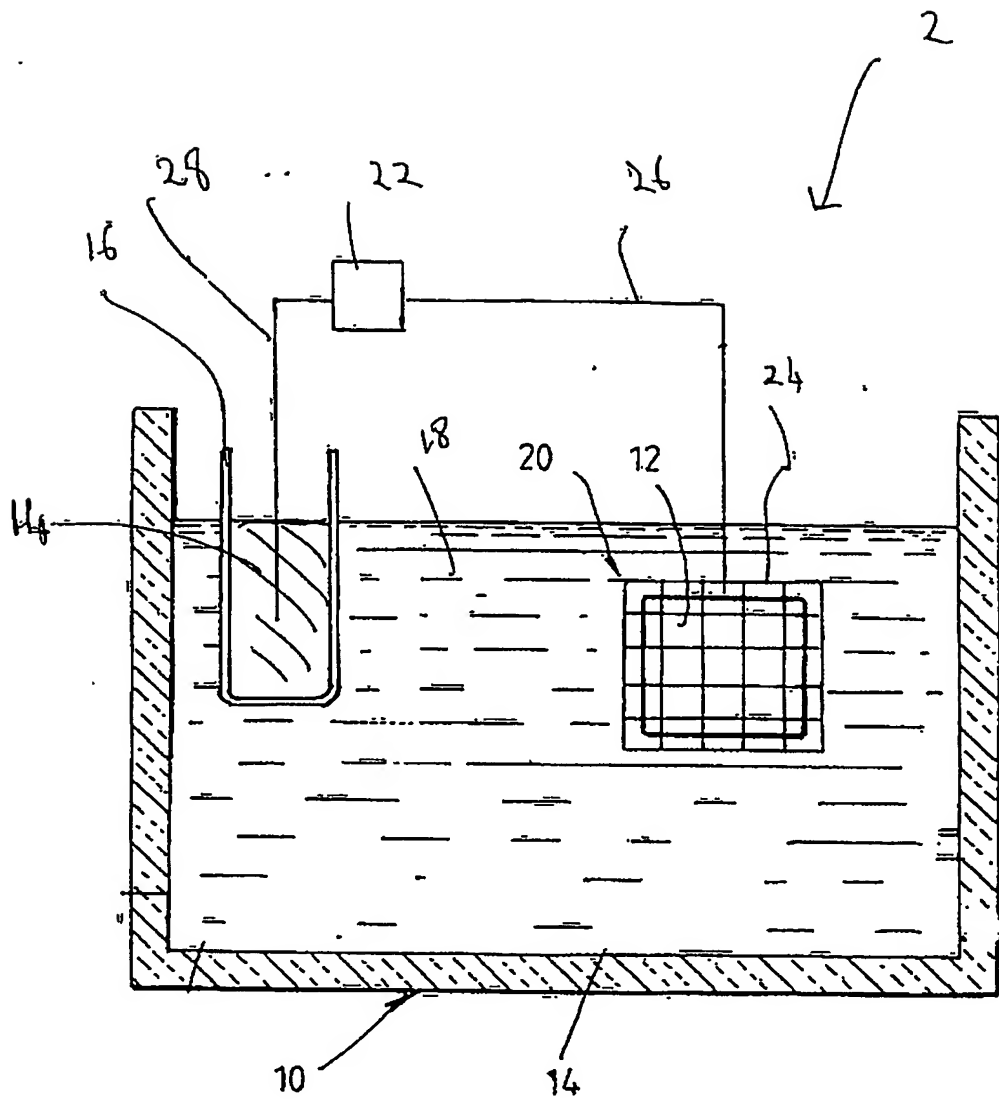
The oxygen that passes into the electrolyte 18 by virtue of electrochemical reduction of the metal oxide is subsequently transported into the molten metal anode 14 via the membrane 16 and dissolves in the molten metal.

15   The dissolved oxygen then oxidizes the steel electrode 28, and iron oxides accumulate on the surface of the molten metal anode and are periodically removed.

20           Many modifications may be made to the preferred embodiment of the present invention described above without departing from the spirit and scope of the invention.

25           By way of example, it is noted that other shapes and configurations of the titania cathode 20 are equally employable, bearing in mind the need to ensure proper electric contact between the power source 22 and the titania to be reduced within the cell.

1/1



III. 1.